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13. ABSTRACT (Maximum 200 words)

The objective of the research project was to conduct a surface microscopic study on the atomic scale of the bonding between an advanced ceramic material and a metal. We have developed surface preparation methods to enable us to routinely obtain atom-resolved scanning tunneling microscopy (STM) images of SiC single-crystals without producing a graphite layer on the surface. Atomic reconstructions of (3 x 3), ($\sqrt{3}$ x $\sqrt{3}$) and (9 x 9) were observed by STM on the 6H-SiC(0001) and (000$\bar{1}$) surfaces. When a metal layer, such as Ti, was deposited on these surfaces, we observed new ($\sqrt{3}$ x $\sqrt{3}$) and ($2\sqrt{3}$ x $2\sqrt{3}$) surface phases which could be correlated to the formation of surface compounds of TiC, Ti_5Si_3, and $Ti_9Si_{12}Ci_{10}$. These compounds probably contribute to the strength of the Ti-SiC joint. During the course of our project, we also investigated the atomic structures of other metal carbide surfaces, namely VC(111), NbC(100) and NbC(110). We also studied the change in surface atomic structure of Si(111) and Si(100) when these surfaces were respectively deformed by a biaxial and a uniaxial tensile stress applied *in situ* in the UHV-STM chamber.

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I. Statement of the Problem Studied

The technological impact of silicon carbide, SiC, covers two distinctly diverse areas: (a) as a high-strength structural ceramic, and (b) as a high-temperature wide bandgap semiconductor. In both of these applications, metallization of the SiC surface is a necessary and important procedure. From the structural point of view, a large complex shape can be produced by joining together parts of small size and simple geometries via a metallic interlayer. From the electronic point of view, good ohmic and Schottky contacts with metals are prerequisites for SiC-based device technology. For both cases, the Ti/SiC system appears to provide desirable results. When the Ti/SiC system is annealed in the temperature range 600-1200°C, phases such as Ti_5Si_3, $TiSi_2$, TiC and Ti_3SiC_2, are reportedly formed [1-6]. Mechanically, these reaction products provide good bonding characteristics to yield a joint of adequate strength; while electronically, the silicide and carbide phases are metallic and thus exhibit rectifying behavior as expected from Schottky barrier diodes.

Both Ti(a = 2.95Å, c = 4.68Å) and 6H-SiC(a = 3.08Å, c = 15.11Å) have hexagonal crystal structures, with a 4% mismatch between the lattice spacings of $(1\bar{1}00)_{Ti}$ and $(1\bar{1}00)_{SiC}$. When Ti was deposited on a 6H-SiC(0001) surface at room temperature, a (1x1) low-energy electron diffraction (LEED) pattern, similar to that of the SiC substrate, was observed. Selected-area transmission electron diffraction (TED) patterns and high-resolution transmission electron microscopy (HRTEM) images [5, 6] of a cross-section of the Ti/SiC interface confirmed pseudomorphic epitaxial growth of Ti on the 6H-SiC(0001) surface. There was no reaction between the as-deposited Ti film and the SiC substrate. Only after annealing at 700°C for 20 min that reaction products of TiC and Ti_5Si_3 were identified [5, 6].

In view of the many interesting properties of the Ti/SiC system, we undertook a scanning tunneling microscopy (STM) investigation on the structure and morphology induced by Ti adlayers on the 6H-SiC(0001) and $(000\bar{1})$ surfaces. STM was particularly useful in following the initial stages of nucleation and subsequent reaction between Ti and SiC when the system was annealed at various temperatures. It was expected that the reaction products would present themselves as different reconstructions on the surface, thereby providing a means of identification of their compositions. The atomic level information provided by STM images would thus lead to an understanding of interface reactions and bonding chemistry between the metal and the ceramic, issues that are central to the metal-ceramic joining process.

II. Summary of the Most Important Results

II.1 STM Studies of Si(100) and Si(111) Surfaces under an Externally Applied Stress

One of the objectives in our research project is to study the strength of the ceramic-metal bond by obtaining an atomistic view with the STM of the SiC surface covered with a metal adlayer under an externally applied stress. It turned out that trying to deform a 6H-SiC(0001) single-crystal wafer with an uniaxial or biaxial stress was both a very difficult and a very costly process, since the expensive wafers fractured easily under an external load. So we decided to test our STM imaging concept with Si(100) and Si(111) wafers.

STM images of strained Si(100) and Si(111) yield very interesting results. A normal Si(100) surface contains equal populations of (2x1) and (1x2) domains. The domain with dimer rows parallel to the step edge is known as Type A domain, while that with dimer rows perpendicular to the step edge is called Type B. When an uniaxial tensile stress was applied to the Si(100) surface at 700°C, the type B domain grew in size at the expense of the type A domain, as observed in previous work [7-10]. We discovered, however, that subsequent annealing of the surface by passing a dc current in either the upstep or downstep direction could affect the population of type A and type B domains. We attributed this to an electromigration effect in which direction of motion of Si atoms on the top surface are influenced by the direction of the heating electric current. A complete description of this effect is given in paper #3 in the publications list.

After the application of a biaxial tensile stress on the Si(111)-(7x7) surface, plastic deformation took place, characterized by the slip of a crystallographic plane in a well-defined crystallographic direction. For Si(111), we identified that the slip plane is the {111} plane. Whenever a slip trace emerges on the surface, it produces a new step, i.e. a glide step, on the surface and is imaged by the STM. We also observed that the strained Si(111) - (7x7) surface contained new (5x5) islands on top of the (7x7) structure. The reason for the islands having a (5x5) structure rather than the (7x7) is not understood since ab initio total energy calculations [11] have shown that the (7x7) is the more energetically favorable structure compared to (5x5). A full description of the *in situ* STM imaging of the strained Si(111) surface is given in paper #5 in the publication list.

II.2 Atomic Structures of 6H-SiC(0001) and (000$\bar{1}$) Surfaces

We were the first research group in the world to successfully obtain atom-resolved STM images on a α-SiC surface. The secret of our success lies in our surface preparation. The surfaces chosen for our study were 6H-SiC(0001) and (000$\bar{1}$) and they were single-crystal

wafers obtained from Cree Research. The samples were cleaned *in situ* in the UHV chamber containing the STM and a heating stage. The sample under study was resistively heated to 850-950°C by passing a DC current through the sample. A flux of Si vapor was directed onto the heated sample surface from a Si evaporator positioned at 15 cm away from the sample. This process removes oxygen contamination from the surface in the form of SiO, a volatile reaction product, while also preventing the formation of a graphite layer by reacting with non-carbidic C to form SiC. Without the presence of the added Si flux, the surface would either be graphite covered, as we have found previously [12, 13], or rough because of the presence of oxide. With our surface cleaning procedure, we were able to obtain atom-resolved STM images of the (3 x 3), ($\sqrt{3}$ x $\sqrt{3}$) and (9 x 9) reconstructions. Structural models were proposed for the (3 x 3) and ($\sqrt{3}$ x $\sqrt{3}$) reconstructions, the details of which were given in paper #7 in the publication list.

II.3 STM Studies of 6H-SiC(0001) and (000$\bar{1}$) Surfaces covered by Ultrathin Ti layers

We used scanning tunneling microscopy (STM) to study the structure, morphology and reaction when ultrathin Ti films (<10 monolayers) were deposited *in situ* on 6H-SiC(0001) Si-terminated and (000$\bar{1}$) C-terminated surfaces. Volmer-Weber growth of Ti islands was observed when deposition was carried out at room temperature. Annealing the surfaces at 700°C produced an ordered ($\sqrt{3}$ x $\sqrt{3}$) phase and a disordered phase on the (0001) surface while the island structure remained unchanged on the (000$\bar{1}$) surface. Further annealing at 850°C caused the ordering of the disordered phase on the (0001) surface into a second ($\sqrt{3}$ x $\sqrt{3}$) phase while the island structure on the (000$\bar{1}$) surface was replaced by large domains of (2$\sqrt{3}$ x 2$\sqrt{3}$) geometry. Structural models were proposed to correlate the observed ordered phases with compositions of the reaction products. We have identified the possible existence of both TiC and Ti_5Si_3 on the (0001) surface. On the (000$\bar{1}$) surface, the (2$\sqrt{3}$ x 2$\sqrt{3}$) surface phase could be either due to a ternary compound with the composition of $Ti_9Si_{12}C_{10}$, or a silicide Ti_3Si_4 if the top-layer C atoms were missing. The details of our determination are presented in paper #8 in the publication list. We were the first in the world to obtain STM images of a SiC surface after the deposition of thin metal films.

II.4 Surface Atomic Structures of Metal Carbides

We have also collaborated with researchers from Europe: M. Hammar from Royal Institute of Technology, Sweden, and M. Schmid, C. Nagl and P. Varga from Techinische Universität Wien of Austria, to determine the surface atomic structures of metal carbides. In the $VC_{0.8}$ (111) case, we determined that the (8 x 1) reconstructed surface consists of a

superposition of a rectangular vanadium layer on top of the hexagonal bulk without any surface buckling. On the $NbC_{0.75}(100)$ surface, STM images show localized areas of a square (1 x 1) structure together with regions of hexagonal structure, indicative of coexisting surface phases. On the $Nb_{0.865}(110)$ surface, a ridge-and-valley grating structure consisting of both (4 x 1) and (5 x 1) geometries was observed over large areas. This type of nanometer scale faceting structure has also been observed in TaC(110) surfaces by other workers [14, 15]. The details of our metal carbide work is given in papers #4 and #9 in the publications list.

III. Publications List

III.1 Papers Published and In Press

1. I.S.T. Tsong. Atomic Level Characterization of Cubic Silicon Carbide Surfaces - A Review. J. Amer. Ceram. Soc. **76**, 269-272 (1993).

2. Y. Wei, M.J. Tsai, J.D. Dow and I.S.T. Tsong. A Straight Domain Boundary of Single-atom Width on a Si(111) - (7 x 7) Surface. Surf. Sci. Lett. **276**, L15-L20 (1993).

3. Y. Wei, W.E. Packard, J.D. Dow and I.S.T. Tsong. Scanning Tunneling Microscopy Studies of Electromigration on Si(100) Surfaces Under External Strain. Non-Destructive Characterization of Materials VI, R.E. Green et al. eds., Plenum Press, New York (1994) 765-772.

4. M. Hammar, B.E. Steele and I.S.T. Tsong. Scanning Tunneling Microscopy Studies of $VC_{0.8}(111)$ - (8 x 1) Surface. Nucl. Instum. Meth. **B85**, 429-434 (1994).

5. Y. Wei, L. Li and I.S.T. Tsong. Surface Morphology of Si(111) - (7 x 7) Under an External Isotropic Tensile Stress. J. Vac. Sci. Technol. **A13**, 1609-1612 (1995).

6. Y. Wei, L. Li and I.S.T. Tsong. Etching of Si(111) - (7 x 7) Under an External Isotropic Tensile Stress. J. Vac. Sci. Technol. **A13**, 1609-1612 (1995).

7. L. Li and I.S.T. Tsong. Atomic Structures of 6H-SiC(0001) and (000$\bar{1}$) Surfaces. Surf. Sci. **351**, 141-148 (1996).

8. L. Li and I.S.T. Tsong. Surface Structure and Morphology Induced by Ultrathin Ti Films on 6H-SiC(0001) and (000$\bar{1}$). Surf. Sci. **364**, 54-60 (1996).

9. R.M. Tsong, M. Schmid, C. Nagl, P. Varga, R.F. Davis and I.S.T. Tsong. Scanning Tunneling Microscopy Studies of Niobium Carbide (100) and (110) Surfaces. Surf. Sci. (in Press)

III.2 Ph.D. Dissertations

Bruce E. Steele, "Impact-Collision Ion-Scattering Spectrometry Studies of Surface Structures". December 1993.

Yi Wei, "Development of Surface Morphology on Silicon Driven by External Stress and Gas Adsorption". May 1995.

Lian Li, "Metal-Induced Reconstructions on Semiconductor Surfaces". August 1995.

IV. Participating Personnel

I.S.T. Tsong - Principal Investigator

W.T. Petuskey - Co-principal Investigator

B.E. Steele - Graduate Assistant - Ph.D. (1993)

Y. Wei - Graduate Assistant - Ph.D. (1995)

L. Li - Graduate Assistant - Ph.D. (1995)

H.W. Shin - Graduate Assistant

S. Chandran - Graduate Assistant

H.D. Lee - Postdoctoral Associate (3-month)

V. Inventions

Title: Hardware and software to control and operate a scanning tunneling microscope (STM)

VI. Bibliography

1.   S. Morozumi, M. Endo, M. Kikuchi and K. Hamajima, J. Mat. Sci. **20**, 3976 (1985).
2.   S.K. Choi, M. Chandrasekaran and M.J. Brabers, J. Mat. Sci. **25**, 1957 (1990).
3.   I.W. Hall, J.L. Lirn, Y. Lepetitcorps and K. BIlba, J.Mat. Sci. **27**, 3835 (1992).
4.   I. Gotman, E.Y. Gutmanas and P. Mogilevsky, J. Mat. Res. **8**, 2725 (1993).

5. J.S. Bow, L.M. Porter, M.J. Kim, R.W. Carpenter and R.F. Davis, Ultramicroscopy **52**, 289 (1993).

6. L.M. Porter, R.F. Davis, J.S. Bow, M.J. Kim, R.W. Carpenter and R.C. Glass, J. Mat. Res. **10**, 668 (1995).

7. F.K. Men, W.E. Packard and M.B. Webb, Phys. Rev. Lett. **61**, 2469 (1988).

8. B.S. Swatzentruber, Y.W. Mo, M. B. Webb and M.G. Lagally, J. Vac. Sci. Technol. **A8**, 2658 (1990).

9. M.B. Webb, F.K. Men, B.S. Swartzentruber and M.G. Lagally, J. Vac. Sci. Technol. **A8**, 2628 (1990).

10. W.E. Packard, N. Dai, J.D. Dow, R.C. Jaklevic, W.J. Kaiser and S.L. Tang, J. Vac. Sci. Technol. **A8**, 3512 (1990).

11. I. Stich, M.C. Payne, R.D. King-Smith, J.S. Lin and L.J. Clarke, Phys. Rev. Lett. **68**, 1351 (1992).

12. C.S. Chang, I.S.T. Tsong, Y.C. Wang and R.F. Davis, Surf. Sci. **226**, 354 (1991).

13. M.H. Tsai, C.S. Chang, J.D. Dow and I.S.T. Tsong, Phys. Rev. B **45**, 1327 (1992).

14. J.K. Zuo, R.J. Warmach, D.M. Zehner and J.F. Wendelhen, Phys. Rev. B **47**, 10743 (1993).

15. J.K. Zuo, D.M. Zehner, J.F. Wendelken, R.J. Warmach and H.N. Yang, Surf. Sci. **301**, 233 (1994).